

# PATENT SPECIFICATION



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380,707

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## COMPLETE SPECIFICATION.

### Improvements in the Separation of Unsaponifiable Matter from Fatty Acid Materials.

We, I. G. FARBENINDUSTRIE AKTIEN-  
GESELLSCHAFT, of Frankfort-on-Main,  
Germany, a Joint Stock Company  
organized under the Laws of Germany,  
5 do hereby declare the nature of this invention  
and in what manner the same is to be performed, to be particularly described  
and ascertained in and by the following statement:—

10 It has already been proposed to separate unsaponifiable constituents, such as alcohols, from fats, oils and waxes, such as wool fat, containing the said constituents by saponification of the saponifiable matter and subsequent distillation while introducing the vapours of inert liquids. This method has the disadvantage that the soaps formed, after expelling the water contained in the material  
15 to be subjected to distillation, become solid with the result that during the further heating a decomposition of at least that fraction of the material to be distilled which is in the neighbourhood of the still walls takes place with the formation of unsaponifiable substances such as hydrocarbons. This is especially the case when it is desired to separate the unsaponifiable constituents of oxidation  
20 products of aliphatic hydrocarbons from the saponifiable constituents. Thus the recovery of unsaponifiable constituents from oils, fats, waxes and the like by this method can only be carried out with a great loss of saponifiable constituents. Moreover, the said method has the disadvantage that it can only be rendered continuous with very great difficulty by reason of the necessity for moving semi-solid to solid residues in and from the stills.

25 We have now found that the separation, by saponification and distillation of unsaponifiable substances from oils, fats, waxes, oxidation products of hydrocarbons and the like can be carried out while protecting the material to be worked to a very great extent by converting the saponifiable constituents within the crude product, before the distillation, into an aqueous mixture of magnesium, calcium and potassium soaps in such relative proportions that the melting point of the

crude saponification product when in the anhydrous state, is below 150° Centigrade. 55

For example the different bases may be added simultaneously or consecutively to the product to be saponified. In the latter case, it is preferable to add the weakest base first and then to introduce the remaining bases according to the degree of their alkalinity. In this manner mixtures of soaps are obtained which melt in an anhydrous state even at slightly elevated temperatures. Thus for example an oxidation product of paraffin wax, saponified in accordance with the present invention and consisting of 7 per cent of potassium soap, 7 per cent of calcium soap, 36 per cent of magnesium soap and 50 per cent of unsaponifiable substances, has a melting point of about 80° Centigrade in the anhydrous state. The preparation of the soap mixtures may also be effected by mixing in suitable proportions different saponification products each of which has been obtained by saponifying with one of the above bases. 70

75 The soap mixtures are subjected to distillation preferably under reduced pressure and while introducing wet, saturated or superheated vapours of inert liquids, such as water, benzene, toluene and the like, or while introducing indifferent gases. When distilling a soap mixture of the said kind, the distillation material remains liquid during the whole period of treatment. Any local overheating and consequent danger of the formation of unsaponifiable substances may be still further strongly reduced by keeping the mass continually in motion, on working at atmospheric pressure, by the introduction of vapours or gases and if desired by stirring. The distilling off of the unsaponifiable substances may also be effected by applying the liquid material to be subjected to distillation in thin layers to heated surfaces, as for example rotating rollers, and exposing them for a short time to the distillation temperature, whereby indifferent gases or vapours may be introduced into the distillation apparatus, if desired, in order to lead away the volatile constituents. After distilling off the unsaponifiable substances by either 90

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of the said methods, the remaining soap mixture, for example from an oxidation product of paraffin wax as described above has a melting point of about  $170^{\circ}$  Centigrade.

A further special advantage of the process according to this invention consists in the fact that the distilling off of the unsaponifiable substances may readily be rendered continuous, as for example may be carried out according to the specification No. 213,267. In this case also a far-reaching protection of the distillation material is ensured by reason of the short duration of the heating.

The difficultly volatile unsaponifiable substances which distil over last of all need not be completely distilled off because they remain to a large extent in the distillation residue remaining in a subsequent purification of the crude fatty acids by steam distillation or by distillation according to the said specification No. 213,267.

The following Examples will further illustrate how the said invention may be carried out in practice, but the invention is not restricted to these Examples.

#### EXAMPLE 1.

The saponifiable constituents within raw wool fat are saponified to the extent of 60 per cent with magnesium oxide and to the extent of 20 per cent each with calcium oxide and caustic potash. The water-containing saponification product is then subjected to distillation, while stirring and while introducing wet steam, at about 30 millimetres (mercury gauge). After expelling the water, the unsaponifiable substances are distilled off from the liquid soaps by increasing the temperature up to  $300^{\circ}$  Centigrade. The distillate consists of 98.5 per cent of unsaponifiable substances while the soaps yield by the addition of dilute sulphuric acid a dark coloured fatty acid mixture having a content of 1.7 per cent of unsaponifiable substances. By a distillation in vacuo with superheated steam, a very pale fatty acid mixture is obtained having an acid value of 195.8, a saponification value of 196.7 and a content of 0.7 per cent of unsaponifiable substances.

#### EXAMPLE 2.

1000 parts of a crude oxidation product of paraffin wax having a saponification value of 146 and containing 45.4 per cent of unsaponifiable substances are saponified to the extent of 70 per cent with 40.5 parts of magnesium oxide and to the extent of 15 per cent each with 12 parts of calcium oxide, 23 parts of caustic potash and 500 parts of water, and then subjected to distillation according to Example 1. The temperature is raised to  $330^{\circ}$  Centigrade. The working up of

the residual soaps is effected as described in Example 1. The crude fatty acid mixture containing 2.5 per cent of unsaponifiable substances yields, after another distillation, a pale fatty acid mixture which only contains 1.4 per cent of unsaponifiable substances. The saponification product may also be subjected to a continuous distillation according to the said specification No. 213,267, at a pressure of 30 millimetres (mercury gauge) and a temperature rising to  $320^{\circ}$  Centigrade. The distillate in this case consists to the extent of 95.3 per cent of unsaponifiable substances. The working up of the resulting soap mixture and purification as described in Example 1 yields a very pale fatty acid only containing 1.6 per cent of unsaponifiable substances.

Instead of distilling the crude soap mixture as described in Example 1, it may be subjected to a distillation by employing rotating rollers. For this purpose the crude saponified oxidation product of paraffin wax is led slowly into a pressure-tight, so-called roller dryer provided with a descending condenser. The material to be subjected to distillation which spreads out on the moving rollers which are rotated in opposite direction and heated to about  $350^{\circ}$  Centigrade gives off in a very short time, at this temperature and at a pressure of about 90 millimetres (mercury gauge), the volatile unsaponifiable substances which are led away by a current of steam superheated to about  $300^{\circ}$  Centigrade which is led over the rollers. The remaining soaps are worked up as hereinbefore described.

#### EXAMPLE 3.

The saponifiable constituents of a brown product containing fatty acids and having the acid value of 147, a saponification value of 169 and a content of 28 per cent of unsaponifiable substances (obtained by distilling the distillation residue of fatty acids from sulphur olive oil) are saponified to the extent of 60 per cent with magnesium oxide and to the extent of 20 per cent each with calcium oxide and caustic potash. The water is expelled from the resulting mixed soap and then the unsaponifiable substances are removed by distillation with steam heated to  $300^{\circ}$  Centigrade and at a pressure of 20 millimetres (mercury gauge), the temperature being gradually raised to  $280^{\circ}$  Centigrade. The remaining mixed soap is worked up as described in Example 1. A dark coloured crude fatty acid mixture having a content of 1.5 per cent of unsaponifiable substances is obtained. A fresh distillation yields a pale yellow odourless fatty acid mixture which has a content of 1 per cent of unsaponifiable substances and from

which a snow-white soap may be prepared.

EXAMPLE 4.

1000 parts of crude beeswax having a saponification value of 101.2 are saponified by heating in an autoclave for 5 hours to about 170° Centigrade (at a pressure of about 8 atmospheres) together with 28 parts of magnesium hydroxide, 8.4 5 parts of calcium hydroxide, 15.7 parts of potassium hydroxide and 500 parts of water, the first two hydroxides thus being employed in a quantity exceeding that theoretically required by 10 per cent and 10 potassium hydroxide in an excess of 5 per cent. A soap is thus obtained in which the fatty acids are saponified to the extent of 70 per cent with magnesium and of 15 15 per cent each with calcium and potassium. The resulting product is then subjected to a continuous distillation by releasing the content of the autoclave through a bottom valve or through an ascending pipe 20 into device for a continuous distillation as described in the Specification No. 213,267 and carrying out the distillation at 260° Centigrade and at a pressure of 40 millimetres of mercury. The soap mixture 25 which is thus freed from unsaponifiable matter to the extent of 212 per cent, remains liquid even at 130° Centigrade. It is then worked up as described in Example 4.

EXAMPLE 5.

1000 parts of crude Carnauba wax having a saponification value of 95.5 are saponified by heating in an autoclave for 40 8 hours to 200° Centigrade (at a pressure of about 16 atmospheres) together with 27 parts of magnesium oxide, 8 parts of calcium oxide, 15 parts of potassium hydroxide and 500 parts of water, the first 45 two hydroxides thus being employed in a quantity exceeding that theoretically required by 10 per cent and potassium hydroxide in an excess of 5 per cent. A soap is thus obtained in which the fatty acids are saponified to the extent of 70 50 per cent with magnesium and of 15 per cent each with calcium and potassium. After the saponification the resulting mass is worked up and subjected to distillation as described in Example 4 while finally heating to 320° Centigrade. The soap then contains 3.4 per cent of unsaponifiable matter and is worked up as described in Example 4.

EXAMPLE 6.

1000 parts of crude sperm oil having a saponification value of 140.5 are saponified by heating in an autoclave for 3 hours, while stirring, to about 170° Centigrade 60 (at a pressure of about 8 atmospheres) to-

gether with 39 parts of magnesium oxide, 12 parts of calcium hydroxide, 23 parts of potassium hydroxide and 750 parts of water, the first two hydroxides thus being employed in a quantity exceeding that theoretically required by 10 per cent and potassium hydroxide in an excess of 5 per cent. A soap is thus obtained in which the fatty acids are saponified to the extent of 70 per cent with magnesium and of 15 per cent each with calcium and potassium. The resulting product is then subjected to a continuous distillation by releasing the content of the autoclave through a bottom valve or through an ascending pipe 70 into device for a continuous distillation as described in the Specification No. 213,267 and carrying out the distillation at 260° Centigrade and at a pressure of 40 millimetres of mercury. The soap mixture 75 which is thus freed from unsaponifiable matter to the extent of 212 per cent, remains liquid even at 130° Centigrade. It is then worked up as described in Example 4.

EXAMPLE 7.

1000 parts of a product of an incomplete hydrogenation of stearic acid according to the specification No. 356,731, and having a saponification value of 135.7 are saponified by heating at atmospheric pressure for 2 hours to 95° Centigrade, while stirring, with the aid of 37.6 parts of magnesium oxide, 11.4 parts of calcium oxide and 500 parts of water. 21.4 parts of potassium hydroxide dissolved in 100 parts of water are then added and heating is continued for further 2 hours, the first two hydroxides thus being employed in a quantity exceeding that theoretically required by 10 per cent and potassium hydroxide in an excess of 5 per cent. A soap is thus obtained in which the fatty acids are saponified to the extent of 70 per cent with magnesium and of 15 per cent each with calcium and potassium. The alcohols set free by the saponification are then distilled off at atmospheric pressure with the aid of superheated steam. The soap mixture which contains 1.3 per cent of unsaponifiable matter is then worked up as described in Example 4. The purified fatty acid can again be subjected to hydrogenation according to the beforementioned process.

EXAMPLE 8.

1000 parts of crude wool fat having a saponification value of 182.7 are saponified with the aid of 43 parts of magnesium oxide, 20 parts of calcium oxide, 37 parts of potassium hydroxide and 500 parts of water, the first two hydroxides thus being employed in a quantity exceeding that theoretically required by 10 per cent and potassium hydroxide in an excess of 5 per cent.

cent. A soap is thus obtained in which the fatty acids are saponified to the extent of 60 per cent with magnesium and of 20 per cent each with calcium and potassium. The resulting aqueous product is then subjected to distillation with wet steam at a pressure of about 30 millimetres of mercury. After removal of the water the unsaponifiable matter is distilled off by slowly raising the temperature to 280° Centigrade. The distillate consists to the extent of 93.5 per cent of unsaponifiable matter, whereas the soap, by decomposition with aqueous sulphuric acid, furnishes fatty acid with a content of 1.7 per cent of unsaponifiable matter. After a distillation in vacuo with the aid of superheated steam a pale fatty acid mixture is obtained which has an acid value of 195.8, a saponification value of 196.7 and a content of unsaponifiable matter of 0.7 per cent.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the separation of unsaponifiable constituents from oils, fats waxes or oxidation products of hydrocarbons containing the said constituents by the saponification of the saponifiable constituents present and subsequent dis-

tillation, which consists in converting the saponifiable constituents within the crude product, before the distillation, into an aqueous mixture of magnésium, calcium and potassium soaps in such relative proportions that the melting point of the crude saponification product, when in the anhydrous state, is below 150° Centigrade.

2. A modification of the process as claimed in claim 1 which consists in mixing in suitable proportions different saponification products of oils, fats, waxes or oxidation products of hydrocarbons each of which has been obtained by saponifying with one of the bases stated in Claim 1, for the production of the mixtures of soaps as claimed in claim 1.

3. The process for the separation of unsaponifiable constituents from oils, fats, waxes or oxidation products of hydrocarbons substantially as described in each of the foregoing Examples.

4. Mixed soaps from oils, fats, waxes or oxidation products of hydrocarbons when freed from unsaponifiable constituents in accordance with the preceding claiming clauses, and the unsaponifiable constituents obtained thereby.

Dated this 15th day of February, 1932.  
J. Y. & G. W. JOHNSON.  
47, Lincoln's Inn Fields, London, W.C. 2,  
Agents.

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